changed by varying the medium, which appears to be approximately true in some acid–indicator base reactions.[12,15]

Acknowledgment.—The sincere thanks of the authors are due to Dr. C. L. Kenny for his support of this work, and to Mr. E. E. Velehradsky for his assistance in making the hydrogen chloride–toluene measurements.

Summary

Measurements are reported of the partial pressure of hydrogen chloride from its toluene solutions over the concentration range 0.015–0.137 molal, and of hydrogen bromide from its solutions in benzene, toluene, *o*-nitrotoluene and *m*-nitrotoluene over the concentration ranges 0.097–0.447, 0.185–0.447, 0.023–0.323 and 0.032–0.449 molal, respectively. The law of Henry is followed in all these solutions, but there is a negative deviation of the hydrogen halide from the law of Raoult. The molal solubilities of hydrogen bromide are greater than those of hydrogen chloride in the solvents considered.

Equilibrium constants for the hydrogen bromide–solvent reactions in the above mentioned solvents and in water are calculated and compared with those of hydrogen chloride–solvent reactions. The apparent relative acidity of the two acids is different in the various types of solvents, and the relative order of acid strengths is reversed in the nitrotoluenes.

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[15] See, *e. g.*, L. P. Hammett and A. J. Deyrup, THIS JOURNAL, **54**, 2721 (1932); D. C. Griffiths, *J. Chem. Soc.*, 812 (1938).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Heat of Neutralization of Sodium Hydroxide with Hydrochloric Acid

BY GERSON KEGELES

Introduction.—Lewis and Randall first undertook the task of tabulating the thermodynamic functions of the elements and their compounds with the ultimate purpose of combining these functions in order to obtain the properties of reactions in which these substances are involved. Their method is equally applicable to reactions in solution, provided the necessary thermodynamic data are known. In the case of solutions of electrolytes, the thermodynamic properties vary extensively with the concentration, and until recently data have been lacking for large concentration ranges. Calorimetric measurements for sodium chloride solutions by Wüst and Lange,[1] Robinson,[2] and Gulbransen and Robinson,[3] and extended thermodynamic studies of hydrochloric acid solutions by Åkerlöf and Teare,[4] and of sodium hydroxide by Åkerlöf and Kegeles,[5] now make it possible to determine the heat of neutralization of sodium hydroxide with hydrochloric acid through 16 molal acid and base at 25°. The results obtained from these separate data agree very well in the lower concentration range with direct calorimetric measurements reported by Richards and co-workers.[6] The heat of neutralization is found to reach very high values at the highest concentrations treated.

Method of Calculation.—The reaction between acid and base of molality m may be expressed as follows

$$[(1)\ \mathrm{NaOH} + (55.51/m)\mathrm{H_2O}] + [(1)\ \mathrm{HCl} + (55.51/m)\mathrm{H_2O}] = \left[(1)\ \mathrm{NaCl} + \left(\frac{1 + 111.02}{m}\right)\mathrm{H_2O}\right]$$

In terms of m, the molality of the resulting sodium chloride is $m' = 55.51m/(111.02 + m)$. The corresponding molal heat of reaction is given by the expression[7]

$$\Delta H = [\overline{H}_{2(m'\ \mathrm{NaCl})} + 55.51/m'\overline{H}_{1(m'\ \mathrm{NaCl})}] - [\overline{H}_{2(m\ \mathrm{NaOH})} + 55.51/m\ \overline{H}_{1(m\ \mathrm{NaOH})}] - [\overline{H}_{2(m\ \mathrm{HCl})} + 55.51/m\ \overline{H}_{1(m\ \mathrm{HCl})}]$$

Upon making the substitutions $\overline{H}_2 = \overline{H}_2^0 + \overline{L}_2$, and $\overline{H}_1 = \overline{H}_1^0 + \overline{L}_1$, and rearranging, the expression becomes

$$\Delta H = \Delta H^0 + [\overline{L}_{2(m'\ \mathrm{NaCl})} - \overline{L}_{2(m\ \mathrm{NaOH})} - \overline{L}_{2(m\ \mathrm{HCl})}] + (55.51/m)[(m/m')\overline{L}_{1(m'\ \mathrm{NaCl})} - \overline{L}_{1(m\ \mathrm{NaOH})} - \overline{L}_{1(m\ \mathrm{HCl})}] \quad (1)$$

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[1] Wüst and Lange, *Z. physik. Chem.*, **116**, 161 (1925).

[2] Robinson, THIS JOURNAL, **54**, 1311 (1932); see also Young and Vogel, *ibid.*, **54**, 3030 (1932).

[3] Gulbransen and Robinson, *ibid.*, **56**, 2637 (1934); see also Young and Machin, *ibid.*, **58**, 2254 (1936).

[4] Åkerlöf and Teare, *ibid.*, **59**, 1855 (1937); see also Harned and Ehlers, *ibid.*, **55**, 2179 (1933), for lower concentrations.

[5] Åkerlöf and Kegeles, *ibid.*, **62**, 620 (1940); see also Harned and Hecker, *ibid.*, **55**, 4838 (1933), for lower concentrations.

[6] Richards and Rowe, *ibid.*, **44**, 684 (1922); Richards and Hall, *ibid.*, **51**, 731 (1929).

[7] The nomenclature of Lewis and Randall ("Thermodynamics") is used here.

where ΔH^0 is equal to the expression $(\overline{H}_1^0 + \overline{H}^0_{2(\mathrm{NaCl})}) - (\overline{H}^0_{2(\mathrm{NaOH})} + \overline{H}^0_{2(\mathrm{HCl})})$, which is the heat of neutralization at infinite dilution, or the negative of the heat of ionization of pure water, as determined by extrapolation of calorimetric heats of neutralization to infinite dilution.

At molalities above $m = 111.02 \cdot 6.156/55.51 - 6.156) = 13.848$, the reaction would produce a supersaturated solution of sodium chloride (solubility = 6.156 at 25°),[8] and solid salt therefore precipitates out. This can be taken account of by adding to the first reaction above, the reaction

$$[(111.02 + m)/55.51m\ (m' - m_{\mathrm{sat.}})]\mathrm{NaCl}_{\mathrm{solution}} = \mathrm{NaCl}_{\mathrm{solid}}$$

giving as the net reaction

$$[(1)\mathrm{NaOH} + (55.51/m)\mathrm{H_2O}] + [(1)\mathrm{HCl} + (55.51/m)\,\mathrm{H_2O}] = \left[(m_{\mathrm{sat.}}/m')\ \mathrm{NaCl} + \left(\frac{1 + 111.02}{m}\right)\mathrm{H_2O}\right] + (1 - m_{\mathrm{sat.}}/m')\mathrm{NaCl}_{\mathrm{solid}}$$

The heat of this reaction is given by the corresponding expression

$$\Delta H = [(m_{\mathrm{sat.}}/m')\overline{H}_{2(\mathrm{sat.\ NaCl})} + 55.51/m'\overline{H}_{1(\mathrm{sat.\ NaCl})}] + (1 - m_{\mathrm{sat.}}/m')H_{\mathrm{solid\ NaCl}} - [\overline{H}_{2(m\ \mathrm{NaOH})} + 55.51/m\overline{H}_{1(m\ \mathrm{NaOH})}] - [\overline{H}_{2(m\ \mathrm{HCl})} + 55.51/m\ \overline{H}_{1(m\mathrm{HCl})}]$$

Upon introducing $\overline{L}_1$ and $\overline{L}_2$ as above, and rearranging, the expression becomes

$$\Delta H = \Delta H^0 + [\overline{L}_{2(\mathrm{sat.\ NaCl})} - \overline{L}_{2(m\ \mathrm{NaOH})} - \overline{L}_{2(m\ \mathrm{HCl})}] + (1 - m_{\mathrm{sat.}}/m')(H_{\mathrm{solid}} - \overline{H}_{2\mathrm{sat.}}) + (55.51/m)[(m/m')\overline{L}_{1(\mathrm{sat.\ NaCl})} - \overline{L}_{1(m\ \mathrm{NaOH})} - \overline{L}_{1(m\ \mathrm{HCl})}] \quad (2)$$

Here the third term represents the heat of crystallization of the precipitated sodium chloride.

The Data.—The relative partial molal heat content of the solute in aqueous sodium hydroxide solutions up to 12 molal at 25° is given according to Åkerlöf and Kegeles by the formula

$$\overline{L}_2 = 837.69\frac{\sqrt{m}}{1 + \sqrt{2m}} - 814054(0.0_{3}6831m - 0.0_{3}2188m^2 + 0.0_{4}1784m^3 - 0.0_{6}602m^4)$$

For the solvent the corresponding expression is

$$\overline{L}_1 = -5.3357\,[(1 + \sqrt{2m}) - 4.6052 \log (1 + \sqrt{2m}) - 1/(1 + \sqrt{2m})] + 14666(0.0_{3}3461m^2 - 0.0_{3}1459m^3 + 0.0_{4}1338m^4 - 0.0_{6}4816m^5)$$

For the range 12 to 16 molal the formulas to be used are

$$\overline{L}_2 = -814054(0.0_{2}14463m - 0.0_{3}586m^2 - 0.0_{6}1293m^3)$$

$$\overline{L}_1 = -54.6 - 4.297m^2 - 0.0_{2}1264m^3$$

In the case of hydrochloric acid, the measurements of Åkerlöf and Teare from 3 to 16 molal lead to similar formulas

$$\overline{L}_2 = 837.69\frac{\sqrt{m}}{1 + \sqrt{2m}} - 814054\,(-0.0_{3}310m - 0.0_{4}558m^2 + 0.0_{5}467m^3 - 0.0_{6}137m^4)$$

$$\overline{L}_1 = -5.3357\,[(1 + \sqrt{2m}) - 4.6052 \log (1 + \sqrt{2m}) - 1/(1 + \sqrt{2m})] + 14666(-0.0_{3}155m^2 - 0.0_{4}372m^3 + 0.0_{4}350m^4 - 0.0_{6}110m^5)$$

Although these authors only measured down to 3 molal, values of $\overline{L}_2$ and $\overline{L}_1$ derived from their formulas at 1 and 2 molal agree with the values reported by Harned and Ehlers[4] sufficiently well so that their formulas may be used over the entire concentration range treated here.

In the case of sodium chloride, the calorimetric data of Robinson and of Gulbranson and Robinson from 0.4 molal through saturated solution were found to follow very closely, the similar formulas

$$\overline{L}_2 = 837.69\frac{\sqrt{m}}{1 + \sqrt{2m}} - 814054(0.0_{3}81389m - 0.0_{3}16582m^2 + 0.0_{4}15481m^3 - 0.0_{6}6823m^4)$$

$$\overline{L}_1 = -5.3357\,[(1 + \sqrt{2m}) - 4.6052 \log (1 + \sqrt{2m}) - 1/(1 + \sqrt{2m})] + 14666(0.0_{3}407m^2 - 0.0_{4}7901m^3 + 0.0_{4}11611m^4 - 0.0_{6}5459m^5)$$

The maximum deviation between the former equation and the experimental data is 5 calories.

The heat of crystallization $(H_{\mathrm{solid}} - \overline{H}_{2\mathrm{sat.}})$ is −380 cal./mole, according to the measurements of Wüst and Lange.[9]

The heat of ionization of water at 25° was taken from the study of Pitzer.[10] The reported value, already given in defined calories[11,12] was re-converted to defined calories, using the more recent data of Osborne, Stimson and Ginnings[13] for the heat capacity of water at 18°. The heat data from the electromotive force measurements are already given in defined calories, and any additional correction in the case of the sodium chloride is negligible. In these units $\Delta H^0 = -13{,}367$ calories/mole at 25°.

The Results.—As calculated from equations (1) and (2), the heat $-\Delta H$ evolved per mole of reacting acid and base at 25° is given at even acid and base molalities and at the saturation concentration in Table I.

[8] This is from the measurements of Wüst and Lange. The "International Critical Tables" give a somewhat lower value, 6.145.

[9] In the notation of Wüst and Lange, this is the saturation heat of solution Λ_s.

[10] Pitzer, THIS JOURNAL, **59**, 2365 (1937); see also study of Rossini, *Bur. Standards J. Research*, **6**, 847 (1931), from which $\Delta H^0 = -13{,}320$ in the same units.

[11] Rossini, *Bur. Standards J. Research*, **6**, 1 (1931).

[12] Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936.

[13] Osborne, Stimson and Ginnings, *Bur. Standards J. Research*, **23**, 197 (1939).

TABLE I

THE HEAT OF NEUTRALIZATION PER MOLE OF REACTING ACID AND BASE

Acid-base molality m	Resulting salt molality m'	Heat evolved $-\Delta H$, in kilocalories (defined)
0	0	13.37
1	0.4955	13.75
2	0.9823	13.97
3	1.4605	14.26
4	1.9304	14.60
5	2.3923	14.98
6	2.8462	15.39
7	3.2924	15.83
8	3.7311	16.27
9	4.1625	16.73
10	4.5868	17.20_5
11	5.0042	17.69
12	5.4147	18.19
13	5.8186	18.73
13.848	6.156	19.15_5
14	(6.2161)	19.23
15	(6.6072)	19.76
16	(6.9922)	20.28

The results are also represented graphically in Fig. 1.

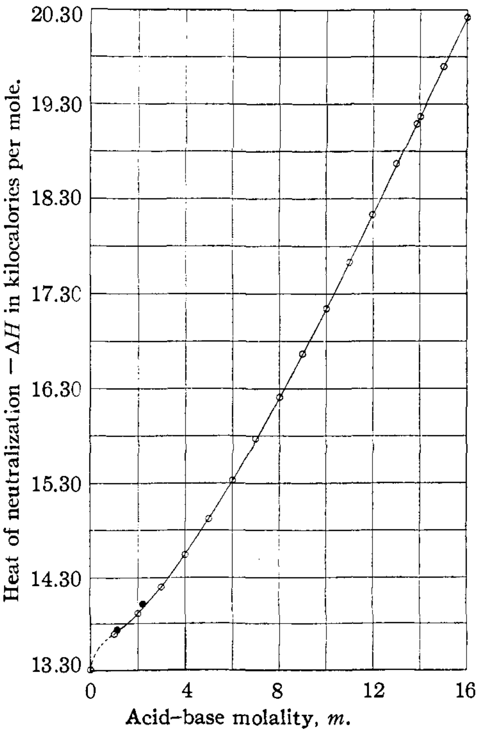

Fig. 1.

Comparison with Measured Values.—Extensive calorimetric studies of the heats of neutralization of a large number of acids and bases have been made by Richards and co-workers. However, for the most part their measurements were made at acid and base concentrations below 1 molal, and at 16 and 20°, at which temperatures accurate heat content data for sodium chloride are lacking at higher concentrations. Two values for sodium hydroxide–hydrochloric acid solutions reported by Richards and Hall[6] at 1.1101 and 2.2202 molal and 20° have been approximately corrected to 25° using the 18° molal heat capacity data of Richards and Rowe,[14] and have been converted from 20° calories to defined calories for the purpose of comparison. An additional correction of 39 calories was made to remove the discrepancy in ΔH^0_{18} values of Pitzer and Rossini and of Richards and Hall. These two values are indicated in Fig. 1 by full-inked circles. They come within 20 and 45 calories of our curve, which is a very good agreement.

Discussion.—It is seen that the deviations of the heat of neutralization from its value at infinite dilution become very large at the higher concentrations. From the form of equation (1), this is seen to be in accord with the observation that the integral heats of dilution of concentrated solutions of hydrochloric acid and sodium hydroxide are very large. Any attempt at a quantitative physical explanation of these phenomena would be entirely premature, however, in the light of the present knowledge of the physics of concentrated solutions of electrolytes. It is to be noted that the break in the curve which would be predicted at the saturation point is so small that at the concentrations treated no change in slope is visible.

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Summary

Separate heat data in the literature for aqueous solutions of sodium hydroxide, hydrochloric acid and sodium chloride at 25°, were combined to give the deviations of the heat of neutralization from its value at infinite dilution. The value at infinite dilution given by Pitzer was reconverted to defined calories and added to these deviations to give the heat of neutralization at even acid–base molalities from 1 to 16. A table of the computed values is included. Very good agreement is obtained at 1.1101 and 2.2202 molal with calorimetric data of Richards and Hall, corrected to 25°.

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[14] Richards and Rowe, THIS JOURNAL, **43**, 770 (1921).